NEXAFS of Siloxane-Based Starburst Dendrimer Network-Based Nanocomposites

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Introduction: There is considerable interest in the development of nanocomposites based on dendrimers as host matrices. The intent is to take advantage of functionalized dendrimer interiors that can complex with an added constituent, resulting in nanocomposites for specific applications. In order to better define such systems, networks based upon radially layered copolymeric siloxane-based dendrimers modified with either Cu^{2+} or Au^{3+} were characterized using near edge X-ray absorption fine structure (NEXAFS). Information on how the added constituent complexes with C, N, and O incorporated within the starburst dendrimer was gained.

Methods and Materials: Crosslinked siloxane-based starburst dendrimer films were prepared from dimethoxymethylsilyl-terminated PAMAMOS dendrimers via moisture hydrolysis of their CH_3O-Si groups followed by condensation of the resulting silanols into interdendrimer siloxy bridges, as reported elsewhwere.[1] Using an *in-situ* preparation method, a methanol solution of desired salt (e.g., $CuSO_4$) was added directly into the solution of precursor PAMAMOS dendrimer in the same solvent, and crosslinking was performed. The samples had a continuous distribution of metal cations at a macroscopic level. NEXAFS was performed on the samples over energy ranges of 250 to 600 eV and 850 to 1050 eV under ultra-high vacuum using the U7A sample station. Observations of the C, N, and O edges and the effects of added the constituents on these edges were made.

Results: NEXAFS Partial electron yields (PEY) for the base dendrimer and their metallic ion-containing equivalents were obtained and their differences were plotted to ascertain the effects and location of the added constituents (See figure below.). The interaction of Cu^{2+} with N and O (and with C at higher concentrations) with increasing Cu concentration is readily discernable.

Conclusions: The splitting of the PEY traces into two groups for the lower and higher concentrations is consistent with the view that the Cu^{2+} preferentially partitions to the dendrimer interiors until a practical limit of about 6 mass % Cu is exceeded. At which point, the Cu distributes throughout the starburst dendrimer network. The results also suggest that NEXAFS can yield information on the interaction of the added constituents with differently bonded N and O within the polymer networks.

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Reference: P.R. Dvornic; A.M. de Leuze-Jallouli; M.J. Owen; S.V. Perz, Chapter 16 in Silicones and silicone-Modified Materials, Clarson, S.J.; Fitzgerald, J.J.; Owen, M.J., Eds.; ACS Symp. Ser. 729, **2000**, pp. 241-269.

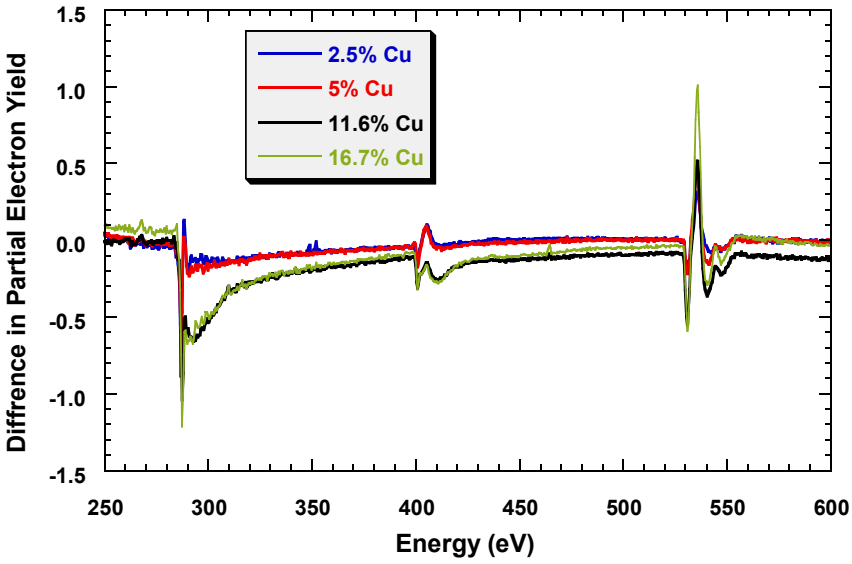

Figure 1. Difference in NEXAFS partial electron yields for Cu^{2+} containing PAMAMOS dendrimer networks as a function of increasing Cu content.